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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE INDUSTRIALISATION OF 14 MeV NEUTRON ACTIVATION ANALYSIS FOR OXYGEN IN STEEL

by

R. Gijbels, J. Hoste and A. Speecke
(University of Ghent)

1969

Report prepared by the University of Ghent - Belgium
Euratom Contract No. 098-66-10 IRAB

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ABSTRACT

A relative method for the determination of oxygen in steel via the $^{16}O(n,p)\ ^{16}N$ reaction by means of 14-MeV neutrons is described. A standard is irradiated immediately behind the sample and the induced activities are counted simultaneously with two separate but identical detector systems. The standard mixture (ca. 5 g of graphite plus iron oxide containing 80 mg of oxygen par g) is compressed into a steel capsule of the same external dimensions as the samples (26 mm diameter, 9 mm thick). Dimensional tolerances, choice and punity control of the oxygen compound and preparation of the standard mixture are discussed. Fast neutron shielding, absorption of fast neutrons, self-absorption of the ^{16}N γ-rays and the average neutron flux in sample and standards are considered and a total correction factor is established. Flux inhomogeneities and differences in counting geometry and discriminator setting can be determined by irradiation and counting of two identical standards. The accuracy of this method was checked by comparison of the results with those of the reducing fusion method; satisfactory agreement was observed, although the activation results tended to be slightly higher. The mean long-term standard deviation for analysis of a given sample over a period of months was found to be $\pm$ 3%.

KEYWORDS

ACTIVATION ANALYSIS
FAST NEUTRONS
OXYGEN
STEELS
DETERMINATION

INTRODUCTION. (*)

Under the impulse of the Bureau Eurisotop of Euratom some three years ago a study was undertaken on the feasibility of 14 MeV neutron activation analysis of oxygen in steel.

This work resulted in a sensitive, fast, reproducible and precise method of analysis and was described in detail in a EUR report "The Determination of Oxygen in Metals by 14 MeV neutron activation analysis" (1). Extensive comparisons were made between the proposed method and the classical reducing fusion methods then in existence. This was carried out under the guidance of the International Comittee for the Study and Rationalisation of the Methods of Gas determination in Iron and Steel - Subcommittee Oxygen. Excellent agreement was obtained and this lead the CECA Authority to sponsor, jointly with the Bureau Eurisotop, the industrialisation of the method in a steelwork.

An improved copy of the original laboratory apparatus was thereafter constructed and installed in the L.D. oxygen-steel work of Cockerill-Ougrée Providence at Ougrée (Liège, Belgium). This company was then introducing a computer program controlled steel elaboration. It was hoped that the oxygen analysis results would be integrated in the production control. This report describes the industialisation of the apparatus together with the encountered difficulties and introduced modifications.

The actual exploitation of the equipment was achieved by a party made up from personnel from the industrial company and from the CNRM (Liège) under the leadership of Dr P. Tyou.

(*) Manuscript received on 3 July 1969.

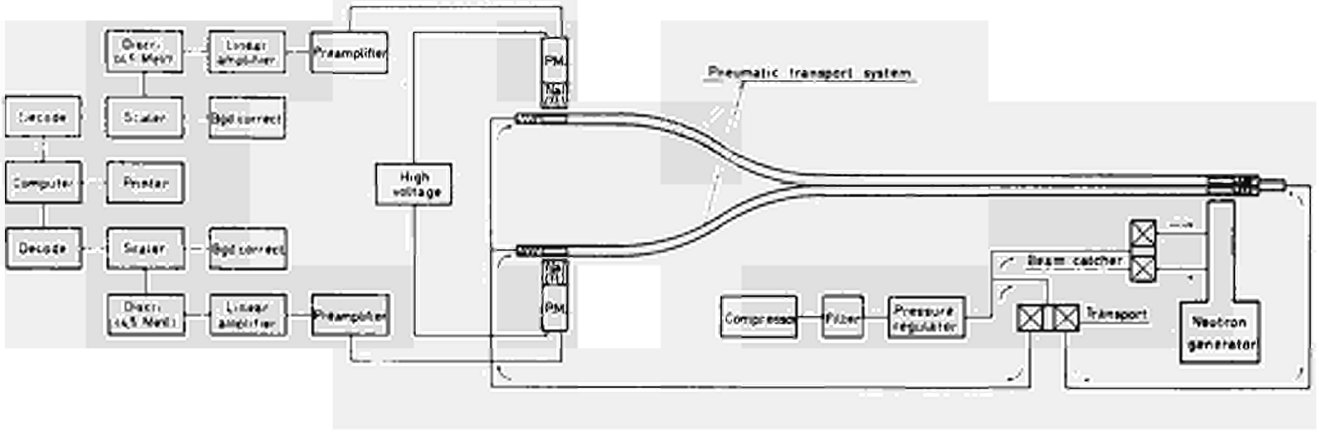

Fig. 1

1. Schematic drawing of the complete apparatus.

APPARATUS.

Except minor changes the apparatus installed in the steelwork is identical to the one used in the original study of the activation analysis of oxygen. Its complete description has been given in detail elsewhere (1). A concise survey however will be given hereafter together with the modifications which have been introduced.

1. Neutron generator.

A SAMES type J neutron generator is used, giving a maximum ion beam of 1.5 mA at 150 kV potential. The 4 Ci tritium targets have a useful diameter of 18 mm. The neutron production is commanded by a tantalum screen, pneumatically taken in and out the deuteron beam. In working conditions, neutron fluxes at the irradiation site of the samples are of the order of 10^9 n/cm^2.sec, and about 5000 irradiations can be achieved with a tritium target. Actually the number of irradiations in the steelwork varied from 4,500 to 6,000.

2. Transport system.

The original study was made on rectangular steel samples with 27 x 7 x 12 mm dimensions. On request of the Oxygen subcommittee of the International Committee for the Study and Rationalisation of the Methods of Gas determinations in Iron and steel, the industrial system has to accomodate cylindrical samples of 26 mm in diameter and 9 mm in thickness, the reason being the easier preparation of these samples from the standard sampling bomb employed in the steel industry. An adequate transport system of the adopted dimensions was therefore constructed from rectangular section aluminium tubes. All advantages of the original idea were kept, esp. the reproducible geometry of irradiation and measurement, and the absence of a sample spinning system.

A schematic drawing of the complete apparatus is given in Fig. 1.

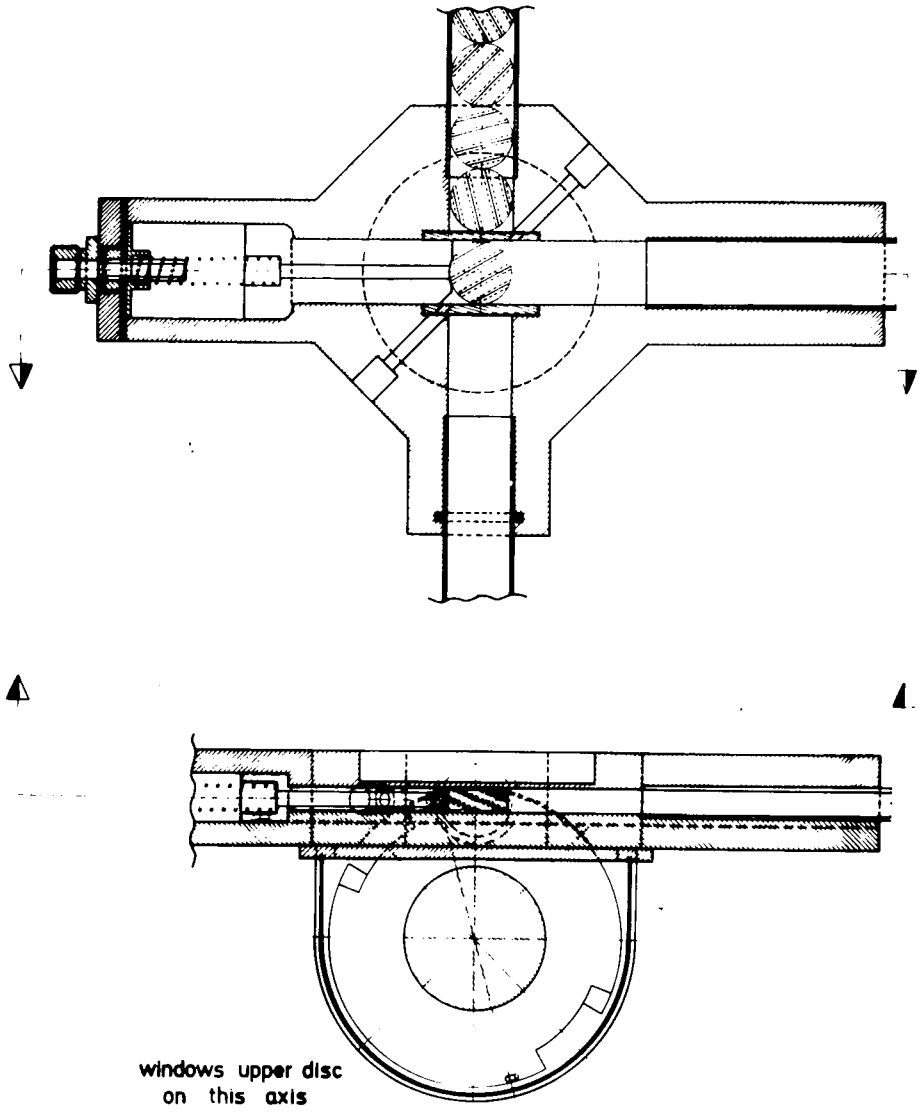

Fig. 2

2. Sample changer.

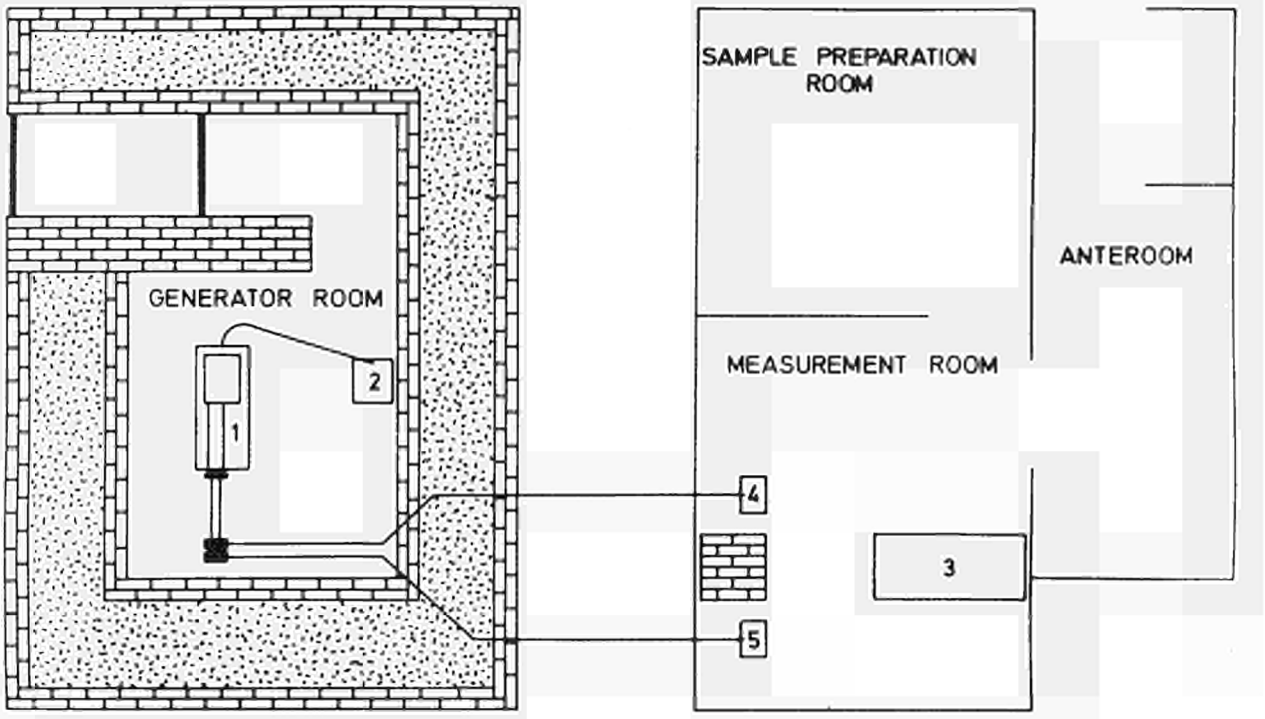

Fig. 3

3. Physical lay-out.

The sample changer incorporated in the system was also a copy of the original one, but did however not stand the wear of industrial exploitation. A new design was conceived where the revolving drum was replaced by 2 rotating discs operating as a window shutter system. The sample changer is represented in Fig. 2.

However a drawback of the new type of samples was the necessity of a new form of standards, as will be explained later.

3. Control system.

The fully automated control system was also applied here, making sequential analyses without manual intervention possible. A minor change however was an electronic computer replacing the previous electromechanical one.

IMPLANTATION AND BIOLOGICAL PROTECTION.

As the ultimate goal of this project was the integration of the oxygen analysis in the production control of the oxygensteel fabrication, the analysis instrumentation was inplanted in the converter hall itself (2).

A site was chosen on the ground level of this hall, 9 m below the working floor. In this way the samples to be analysed were easily conveyed by gravity to the sample preparation room. However, as the neutron generator was thus to be installed in a space accessible to the steel production workers, very stringent health physics rules were applied.

As is shown in Fig. 3, a concrete bunker was created to house the accelerator. The building material was slag-bricks and light concrete. The walls has a thickness from 1.20 to 1.50 m. The roof of the building in reinforced concrete was only 0.5 m thick, which was sufficient as the location was thus chosen that is was impossible to approach the building from above for less than 10 m.

The measurement room was constructed separately from semi-permanent material and houses also the sample preparing equipment.

A neutron density survey was carried out in the most exposed points, with a callibrated BF_3 counter. The shielding provided proved to be very adequate to the extent that the use of personnel neutron dosimeters was no longer warranted. Typically at maximum neutron output, a neutron flux of less than the detection limit, 3 $n/cm^2/sec$, was measured in the counting room.

PROBLEMS ENCOUNTERED AT THE INDUSTRIAL EXPLOITATION OF THE OXYGEN ANALYSIS EQUIPMENT.

The transposal of a laboratory apparatus into an industrial equipment caused several difficulties to appear. They were due to different reasons, but mostly to the less favourable surroundings encountered in a L.D. converter hall.

1. The industrial environment.

The measurement room being exposed to the very large temperature changes in an open factory hall, an airconditioning system ($\pm$ 1°) had to be installed keeping the stability of the counting equipment within reasonable limits. Also the very heavy dustburden of the atmosphere (esp. ironoxide, graphite) caused several difficulties, eliminated by addition of an anteroom and installation of filters in the airvents.

The rather frequent explosions encountered in the converter hall proved very troublesome; one of these caused a breakdown in the 150 kV high voltage supply and destroyed a photomultiplier tube in one of the detectors. Thereafter all equipment was installed on shock absorbers which proved to be highly successfull.

2. Man power.

Although the analysts working with the apparatus had a complete lack of nuclear knowhow, the full automatisation of the instrumentation and the simplicity of the proposed method neccessitated only a very short running-in period. In a relatively short time therefore reliable results could be produced.

3. Sample preparation.

As in the production control of the steel conversion the time factor is of extreme importance, the preparation and finishing of the samples had to be reduced to a minimum. With the help of custom-made cutting tools the time necessary for the preparation of the samples from a red hot bomb sampling could be reduced to 45 sec on a heavy duty lathe. The rather coarse surfaces of the samples however caused a more than normal wear of the transportation system, esp. the nylon bumpers at the irradiation and measurement stations suffered heavily; their replacement however is very easily performed.

The excessive wear and tear on the sample changer necessitated the design of a new changer, as has been stated previously. Also lately the industrial user of the analysis system is considering further improvements of the sample preparation with a gain in time and quality.

STANDARDS.

Oxygen standards as had been used in the laboratory apparatus for the rectangular shaped samples could not be adopted for the industrial system. For the cylindrical samples, boxes were machined from ordinary steel with outer dimensions of 26 mm diameter and 9 mm thickness. The void volume of the boxes was 22 mm in diameter and 7 mm thickness. Filling-up this volume with an oxygen standard, such as oxalic acid, benzoic acid or ferric oxide, was not allowed, because of the high amount of oxygen present. This would indeed have caused an excessive ^{16}N-activity, overloading the counting apparatus. Therefore a diluting medium was necessary and finally a mixture of spectroscopic graphite - iron oxide was adopted, with a total oxygen content of about 400 mg.

Several problems however came into existence by this procedure. The well known axial and lateral flux gradients (1) around neutron generators imposed corrections for the non homogeneous distribution of the oxygen in the standards.

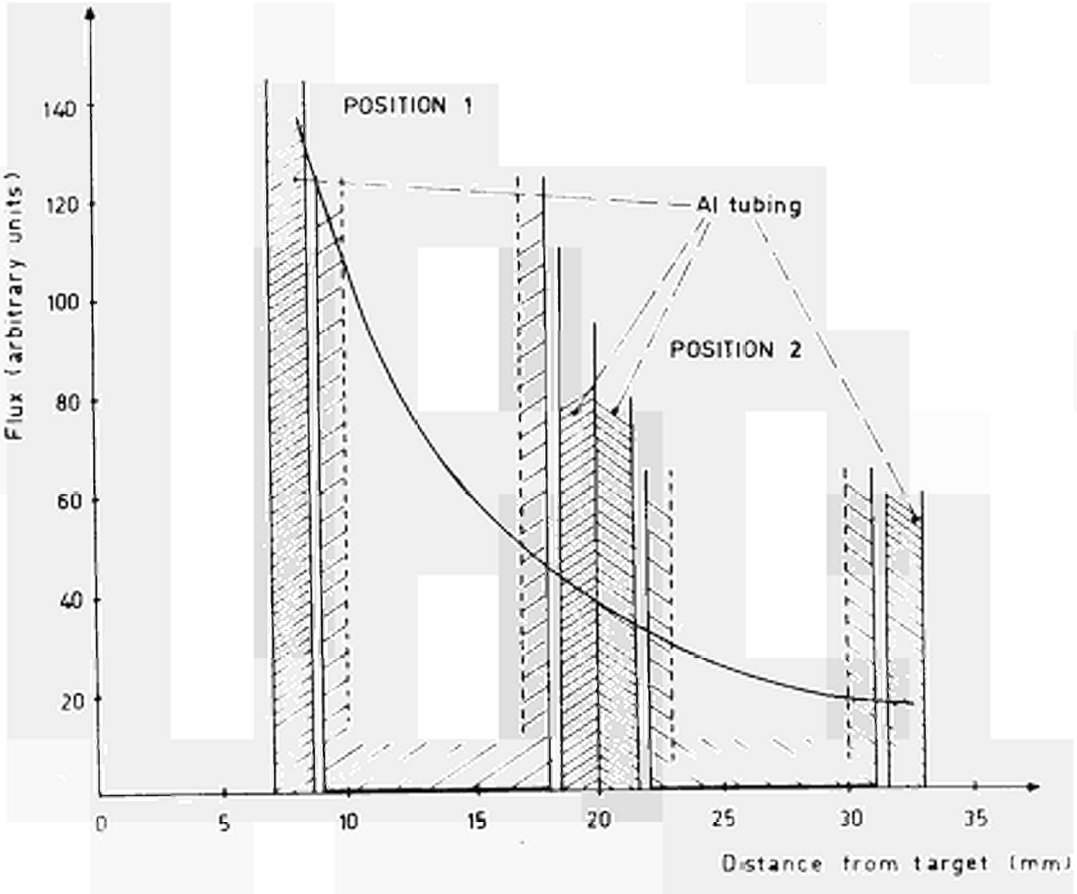

Fig. 4

4. Axial flux gradient.

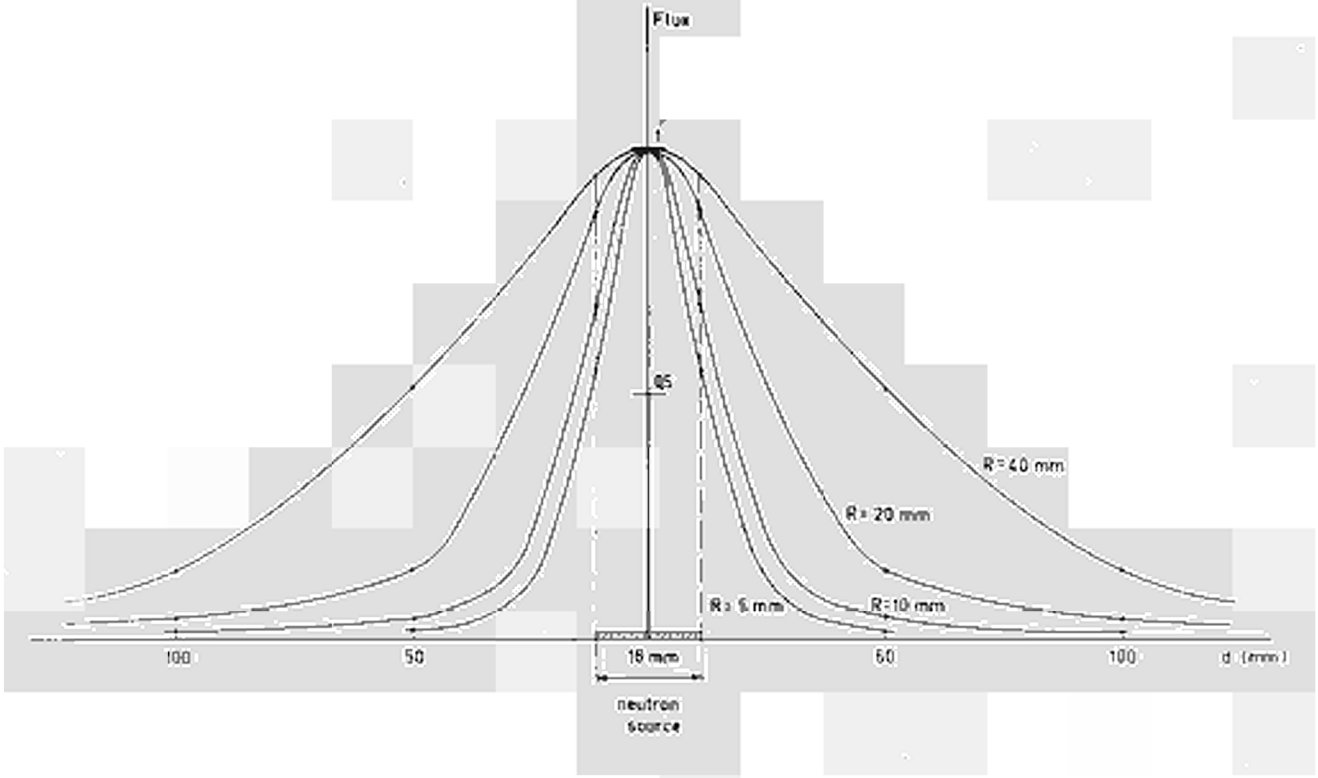

Fig. 5

5. Lateral flux gradient.

But also nuclear properties such as γ-adsorption, total neutron removal cross section had to be carefully investigated. They caused indeed important differences to appear in the specific ^{16}N activities in sample and standard. This effects could be neglected in the standards used in the laboratory equipment, where only about 15% of the total steel was removed for the introduction of the oxygen bearing material. In the cylindrical standards however, about 55% of their volume is taken up by non steel material (3).

1. Axial and lateral flux gradients.

Important axial and lateral flux gradients exist at the irradiation position as appears from Fig. 4 and 5. Consequently, the specific activity produced by irradiation in the standard (position 2) will be lower by a factor of 3 to 4 than that in the sample. To minimize the statistical error in counting A_s, the standard must contain a sufficient amount of oxygen, e.g. between 300 and 400 mg. Moreover, the oxygen in the standards must be as homogeneously distributed as possible. However, steel with such a high accurately known oxygen content is not available. Nylon, plexiglass, etc., cannot be used since their oxygen content is not sufficiently well known and is not always homogeneously distributed.

Therefore, the standards used in this work were cylindrical capsules in ordinary steel, machined to the following dimensions (see Fig. 6): internal diameter 22.0 $\pm$ 0.02 mm, internal thickness 7.00 $\pm$ 0.02 mm ; external diameter 26.0 mm and external thickness 9.00 $\pm$ 0.02 mm. The wall thickness of bottom and cover should be 1.00 $\pm$ 0.01 mm. These tolerances must be kept as strictly as possible, as appears from the following examples. A standard with walls of 0.79 and 1.42 mm for cover and bottom respectively gave rise to a difference of 15% in measured activity (normalized to the same flux) when irradiated with either side towards the target. For walls of 0.65 and 1.15 mm, this difference was 11%; for 0.87 and 1.14 mm, 5% ; for 0.97 and 0.99 mm, 2% (see also Table I).

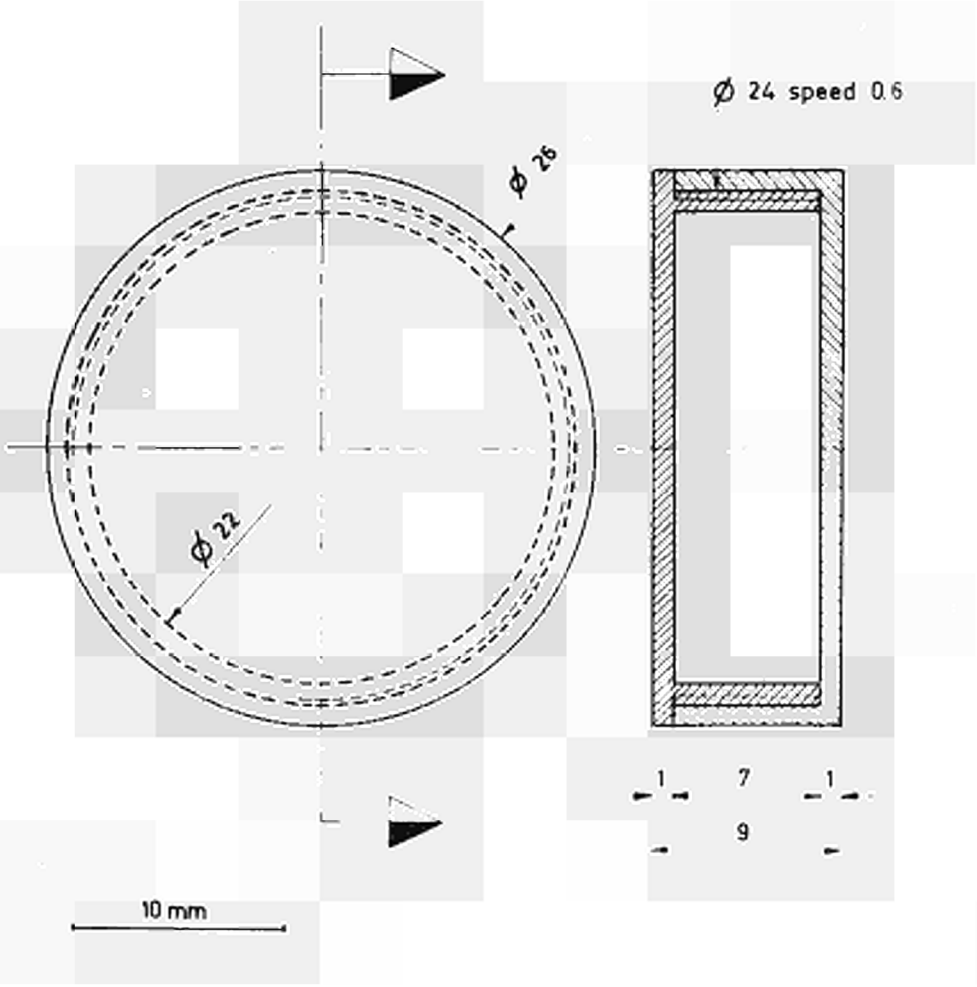

Fig. 6

6. Standard capsule.

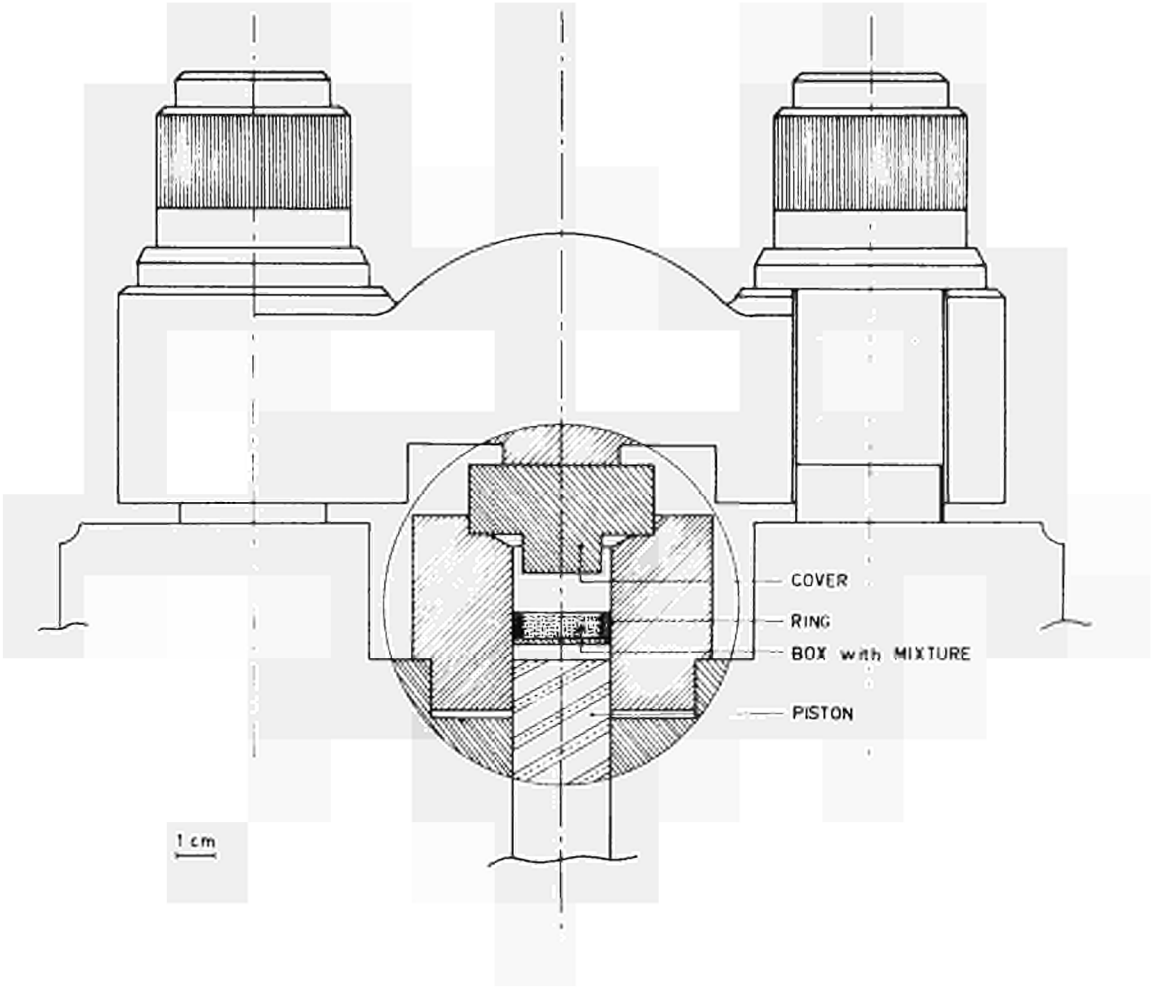

Fig. 7

7. Pressing of the standard mixture in the capsule.

The relatively large volume of these capsules does not allow a complete filling with a homogeneous and pure substance of known oxygen content, since the induced ^{16}N activity will overload the counting apparatus. A mixture with graphite (National spec pure, grade SP-1 suitable for pressing pellets) is proposed, as this substance is available in very high purity and does not give rise to interfering activities; it has a small blank value (oxygen content) and is suitable for making pellets. This mixture is directly pressed into the capsules, see Fig.7.

2.Choice of oxygen compound.

Oxalic acid $(COOH)_2.2H_2O$, an acidimetric and oxidimetric primary standard is not available as a finely divided powder and cannot directly be mixed with graphite. Moreover, partial dehydration is possible because of local heating during grinding. Benzoic acid primary standard is finely divided but shows a tendency to "coagulate" after pressing, even after thorough mixing with graphite. Finally iron(III) oxide was chosen since it is a very finely divided powder of definite composition; it can be mixed homogeneously with graphite and is easily pressed into pellets.

3. Purity control of iron oxide standard.

Iron(III) oxide (Fe_2O_3 pro analysi, Merck; Urtitersubstanz zur Eisenbestimmung mit $KMnO_4$ in salzsaurer Lösung) was used. Gravimetric analysis with urea and ignition of the hydroxide at 700° to constant weight yielded 100.25% (average value of 3 determinations) of the weighed sample.

The homogeneity after mixing with graphite was checked as follows : ca. 200 mg of the mixture was boiled for 30 min with 3 ml of concentrated hydrochloric acid, the graphite was filtered off, and iron was precipitated with ammonia and urea; the precipitate was also ignited at 700°. For 3 determinations, differences varying from 0 to -0.3% (i.e. 0 to 0.13 mg) were found between the theoretical and experimental values.

These data show that, in the most unfavourable case, the compound used should contain 98.4% Fe_2O_3 and 1.60% FeO, i.e. the oxygen can be too low by at most 0.4%.

4. Preparation of the mixture.

Mix 11.0075 g of graphite and 3.9925 g of Fe_2O_3 homogeneously by shaking with plexiglass beads for at least 45 min. The mixture thus contains 26.62% Fe_2O_3 or 80.00 mg of oxygen per g. Fill the bottom of the capsule with the mixture (see Fig. 7); after pressing for 20 sec at 1000 psi, remove the cover, fill the box again, and press under the same conditions. Repeat this procedure until the box is completely filled, i.e. ca. 7 times. At this stage the homogeneity of the mixture can be checked by observing the surface of the pellet with a microscope (8 x 10). Two standards having the same thickness (wall 1.00 mm, pellet 7.00 mm) can be observed with the same focussing. After weighing, grease the screw thread with vaseline and close the capsule.

The box contains 4.92 g of the mixture, i.e. 394 mg of oxygen. The blank value of a box, filled with a pure graphite pellet, was 4.3-4.5 mg of oxygen as determined by activation analysis.

To be of practical value, a standard must be completely symmetrical ; both sides facing the tritium target, must yield the same activity. Moreover, two identical standards should be available, in order to determine the k-factor (see below). This was checked by irradiating two standards and counting the induced ^{16}N activity. Some typical results are given in Table I. The data show that the standards are identical and symmetrical, hence they are completely interchangeable and reversible. Note that this also eliminates manipulation errors.

TABLE I.

Comparison of two oxygen standards .

Position 1	Position 2	k [a]
St. 1 (c)	St. 2 (c)	4.00 ± 0.04 [b]
St. 1 (c)	St. 2 (b)	4.00 ± 0.04 [b]
St. 2 (b)	St. 1 (b)	4.00 ± 0.04 [b]

a ratio of measured ^{16}N activities;

b average value of 20 determinations; the reproducibility is expressed in terms of the standard deviation for a single determination;

(b) bottom side facing the tritium target;

(c) cover side facing the tritium target.

5. Theoretical considerations. Calibration of the system (determination of k).

At the end of the irradiation, the measured ^{16}N activity for a standard irradiated in position 1 (nearest to the target) is given by

$$A_s(I) = \sigma \left[\bar{\varphi}_1\right] w_s \theta N_A SC_s C_1/M \qquad (1)$$

where σ = 14 MeV cross section of the reaction $^{16}O(n,p)^{16}N$;

θ = isotopic abundance of ^{16}O;

N_A = Avogadro's number;

M = atomic weight of oxygen;

S = saturation factor = $1 - \exp(-\lambda t_b)$;

$\left[\bar{\varphi}_1\right]$ = average 14 MeV neutron flux in the capsule at position 1 (diameter 22 mm, thickness 7 mm);

C_1 = detection efficiency, including the setting of the discriminator and the detection efficiency of the detector for the γ-rays of interest at measuring station 1;

C_s = "transmission factor", which takes into account the absorption of neutrons in the standard during activation and the self-absorption of γ-rays during the counting.

The measured activity for a standard, irradiated in position 2 is given by

$$A_s(2) = \sigma \left[\bar{\varphi}_2\right] w_s \theta N_A S C_s C_2 \exp(-\Sigma_s d)/M \qquad (2)$$

where $\left[\bar{\varphi}_2\right]$ is the average 14 MeV neutron flux in the box at position 2. The factor $\exp(-\Sigma_s d)$ takes into account the 14 MeV neutron absorption by a

simultaneously irradiated standard in position 1. Σ_s is the macroscopic cross-section for effective removal of fast neutrons for 2 mm of steel plus 7 mm of graphite mixture ; d = 9 mm.

The absorption of neutrons and γ-rays in both the standards is the same (C_s). Discriminator setting and counting geometry for measuring station 2 are taken into account by C_2.

The measured activity ratio k is given by

$$k = A_s(I)/A_s(2) = \left[\bar{\phi}_1\right] C_1 / \left[\bar{\phi}_2\right] C_2 \exp(-\Sigma_s d) \qquad (3)$$

6. Oxygen analysis in steel.

The measured ^{16}N activity, induced in a steel sample, irradiated in position 1, is given by :

$$A_{Fe}(I) = \sigma \bar{\phi}_1 w_x \theta N_A S C_{Fe} C_1 / M \qquad (4)$$

where $\bar{\phi}_1$ = the average flux in a cylinder of 9 mm thickness and 26 mm diameter (dimensions of the steel sample);

w_x = the unknown oxygen weight in the steel sample;

C_{Fe} = the "transmission factor" for steel.

For the standard, which is irradiated simultaneously in position 2, one can write :

$$A_s(2) = \sigma \left[\bar{\phi}_2\right] w_s \theta N_A S C_s C_2 \exp(-\Sigma_{Fe} d)/M \qquad (5)$$

since the standard is shielded by a steel sample. Σ_{Fe} is the macroscopic fast-neutron removal cross-section for iron and d = 9 mm.

From eqns. (4) and (5), one obtains

$$\frac{A_{Fe}(1)}{A_s(2)} = \frac{\bar{\phi}_1 w_x C_1 C_{Fe}}{\left[\bar{\phi}_2\right] w_s C_2 C_s \exp(-\Sigma_{Fe} d)} \qquad (6)$$

After multiplying nominator and denominator by $[\bar{\phi}_1]$ and substituting eqn. (3) into eqn. (6), one obtains

$$w_x = \frac{w_s}{k} \cdot \frac{A_{Fe}(1)}{A_s(2)} \cdot \frac{C_s}{C_{Fe}} \cdot \frac{\exp(-\Sigma_{Fe} d)}{\exp(-\Sigma_s d)} \cdot \frac{[\bar{\phi}_1]}{\bar{\phi}_1} \qquad (7)$$

k is determined experimentally in step (i); $A_{Fe}(1)$ and $A_s(2)$ are determined experimentally in step (ii); w_s is known, namely, 394 mg of oxygen, not including the blank value. Calculation of w_x is possible, if C_s/C_{Fe}, $\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_s d)$ and $[\bar{\phi}_1] / \bar{\phi}_1$ are known.

7. Experimental determination of $\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_s d)$.

In position 2 an oxygen standard is irradiated and its activity measured with a steel sample or an oxygen standard in position 1. The neutron output is measured by means of a BF_3 counter, surrounded by 5 cm of paraffin wax. This setup allows the determination of the ratio of the fast-neutron removal for a steel sample of 9 mm thickness to that for a standard (2mm steel plus 7 mm graphite-iron oxide mixture).

The average value for 6 x 20 determinations was found to be

$$\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_s d) = 0.949 \pm 0.006 \text{ (s.d. of the mean).}$$

It should be noted that no measurable difference was observed between steel and stainless steel.

8. Experimental determination of C_s/C_{Fe}.

This ratio includes both the absorption of 14 MeV neutrons in the sample during activation and the absorption of the γ-rays of ^{16}N during the counting. It can be considered as a transmittance factor (12).

Seven steel disks, 22.0 mm in diameter and 1 mm thick and cellophane foils of the same diameter were alternately piled to a height of 7 mm and placed in a standard capsule.

Afterwards, seven aluminium disks 22.0 mm in diameter and 1 mm thick and the same cellophane papers (on the same place in the capsule to avoid differences due to inhomogeneities in the cellophane) were used.

These samples were consecutively irradiated in position 1, while the neutron flux was monitored with a BF_3 counter. After correction for the blank value of capsule and Fe or Al disks (i.e. without cellophane), the following ratio was found

$C_s/C_{Fe} = 1/(0.939 \pm 0.005)$ (s.d. for the average value of 7 x 20 determinations).

Aluminium was used instead of the graphite-Fe_2O_3 mixture, because the latter contains too much oxygen. Pure graphite could not be used, since it is very difficult to make layers of exactly 1 mm between two successive cellophane disks.

The use of aluminium in the cylindrical iron capsule is justified, as its absorption for 14 MeV neutrons equals that of the graphite-Fe_2O_3 mixture within ca. 1%, in agreement with the calculated value (cf. $\exp(-\Sigma_{Al}d)/\exp(-\Sigma_s d) = 1.012$ for a pure aluminium sample and an oxygen standard). For C_{Al}/C_s one calculates in a similar way as above, $560.5/565.45 \simeq 0.99$ using $d = 0.13$ g.cm^{-2} for a 0.1 cm layer of the mixture, and $\mu_d \simeq 0.026$ cm^2.g^{-1}.

The absolute error caused by replacing the graphite-iron oxide mixture with aluminium is thus estimated to be about 1% ($I/(0.939 \pm 0.01)$).

9. Experimental determination of $[\vec{\Phi}_1]/\bar{\Phi}_1$.

This ratio takes into account the different 14 MeV "neutron density" in a capsule (internal diameter 22.00 mm, thickness 7.00 mm) and in a normal sample (diameter 26.0 mm, thickness 9.0 mm). The factor actually takes into account two factors.

(a) Decrease in thickness.

As can be seen from Fig. 4 this decrease (9.00 mm - 2 x 1.00 mm = 7.00 mm) lowers the average 14 MeV "neutron density", and thus the specific activity. Its contribution was determined as follows : 7 steel disks (22.0 mm in diameter and 1 mm thick) are placed in a standard capsule and irradiated in position 1 (see Figs. 1 and 4). After irradiation the induced ^{56}Mn activity of each disk is measured on a flat 3 x 3" NaI(Tl) detector. The measured activity, corrected for decay, is directly proportional to the flux and is plotted as a function of distance from the target (cf. Fig. 4). The average flux in the capsule is $(\sum_1^7 A_i)/7$ arbitrary units. Extrapolation 1 mm towards and 1 mm away from the target allows calculation of the average flux over a sample of 9 mm thickness, namely $(\sum_1^9 A_i)/9$ arbitrary units.

Similar series of experiments were done with 7 steel disks (26 mm in diameter and 1 mm thick) placed symmetrically in the pneumatic tube at position 1. The same result was found.

Average value $\sum_1^7 A_i/7 \Big/ \sum_1^9 A_i/9 = 0.974 \pm 0.001$.

(standard deviation of the average of 11 series of measurements).

(b) Decrease in radius.

As can be seen from Fig. 5, the decrease in radius (13.00 mm - 2.00 mm = 11.00 mm) increases the average 14 MeV "neutron density", and thus the specific activity of ^{16}N in the capsule.

This contribution was determined as follows : steel disks (26 mm in diameter and 1 mm thick) were irradiated and the central parts (22 mm diameter) cut out. The resulting disks and rings were dissolved in hydrochloric acid, the solutions diluted to 25 ml and the ^{56}Mn activity measured. After decay corrections, the ratio (sum of specific activities of central parts)/(sum of specific activities of central parts + rings) was computed. The average value was 1.070 ± 0.005 (standard deviation of the average of 9 determinations).

The most important factor, which makes the measured specific ^{16}N activity different in standards and samples, is the radial contraction. Note that the factor $\exp(-\Sigma_{Fe} d)/\exp(-\Sigma_s d)$ and C_s/C_{Fe} approximately compensate each other. The overall correction factor is

$$\frac{(0.949 \pm 0.006)}{(0.939 \pm 0.005)} (0.974 \pm 0.001)(1.070 \pm 0.005) = 1.053 \pm 0.01$$

Hence the amount of oxygen in the steel sample can be calculated from the following equation :

$$w_x = \left\{(1.053\, w_s + b)/k\right\} \cdot \left\{A_{Fe}(1)/A_s(2)\right\} \quad (8)$$

The relative error of the correction factor 1.053 is ca. 1%. The absolute systematic error is estimated to be within the same limits. For a standard containing 394 mg of oxygen (as Fe_2O_3 in graphite), this means that the apparent oxygen weight which has to be used for oxygen analysis in steel is (394 mg x 1.053) + 4.3 mg or 419.2 mg ; 4.3 mg is the blank value for the steel capsule and for the graphite.

RESULTS.

1. Accuracy tests on the standard. Comparison between activation analysis and reducing fusion.

The oxygen content in 6 different steel samples was determined by activation analysis (A.A.) and the results compared with those obtained by reducing fusion analyses (R.F.A.) in three of four selected laboratories of the C.E.C.A. High Authority. Results are given in Table II. For each laboratory the average value of these reducing fusion analyses is given. The overall average value is also indicated with the standard deviation for a single determination. In the case of activation analysis, the average value of 9 analyses is given; the ca. 35 g disks were analyzed on both sides, but no substantial heterogeneity was observed.

The agreement of the results obtained by the two methods is satisfactory, although there is a tendency to find higher results with activation analysis (see samples 1 and 2).

TABLE II.

Comparison between results of activation analysis and fusion analysis (in p.p.m. oxygen).

Sample	R.F.A. average value for				R.F.A.*	A.A. *	A.A.-
	Lab.I	Lab.A	Lab.E	Lab.M	overall average	average	R.F.A. (p.p.m.)
1	269	265	254	-	263±8	285±17	+ 22
2	169	145	149	-	154±13	183±12	+ 29
3	146	144	137	-	142±7	148±7	+ 6
4	322	329	301	-	317±25	316±15	- 1
57	943	910	952	901	929±27	935±25	+ 6
68	1230	1205	1275	1233	1240±35	1253±40	+ 13

* = standard deviation for a single determination.

2. Instanteneous reproducibility.

As has been explained elsewhere (1) the reproducibility error of the activation analysis results is made up of two contributions. Firstly as in all radioactivity measurements the square root of the number of counts registered. In the procedure under discussion, this error is mainly based on this counts obtained from the sample to be analysed. Secondly an "apparatus error" of the order of 1.5 to 2%, caused primarly by geometry factors.

In the industrial equipment where samples of 36 g are analysed, compared to 18 g previously, it is obvious that for a given concentration a double activity will be measured, all parameters being constant, thus lowering the error due to the radioactivity by a factor of $\sqrt{2}$ or about 1.4. The "apparatus error" of the industrial equipment also seems to be somewhat lower, due to a better mechanical construction.

Typical errors on the reproducibility for 1 analysis, calculated from 10 results are 7% for 80 ppm
3,5% 600 ppm
2% 1200 ppm samples.

3. Long term reproducibility.

Sample 57 (a chromium-manganese steel) was regularly analyzed over a period of 6 months, using the same oxygen standard. The results are given in Table III. Each value is the mean of 5 determinations, the standard deviation for a single determination is given. It can be seen that essentially the same result was found over a long period, the average value being 941 p.p.m.

TABLE III.

Long-term reproducibility (results for sample 57-front side).

Date	p.p.m. oxygen	Date	p.p.m. oxygen
30-06-67	933 ± 13	09-11-67	936 ± 21
03-07-67	943 ± 36	09-11-67	936 ± 13
04-07-67	929 ± 27	17-11-67	944 ± 45
04-10-67	951 ± 22	23-11-67	946 ± 35
10-10-67	950 ± 20	23-11-67	934 ± 35
25-10-67	944 ± 15	07-12-67	915 ± 47
25-10-67	944 ± 15	07-12-67	944 ± 45
27-10-67	936 ± 40	08-12-67	949 ± 26
27-10-67	931 ± 37	13-12-67	934 ± 43
30-10-67	934 ± 17	14-12-67	945 ± 55

Mean long-term standard deviation : ± 30 p.p.m. (± 3.2%)

Lowest value ± 13 p.p.m. (± 1.4%)

Highest value ± 55 p.p.m. (± 5.8%)

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1. D.De Soete, J.Hoste, A.Speecke; The determination of oxygen in metals by 14 MeV neutron activation analysis. EUR 3565e, Brussels (1967).
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The willingness to accept and the help in establishing an entirely new method in its steel plant, shown by Cockerill-Ougrée-Providence, is highly appreciated. Especially Mr Grosjean, Director, Mr Lacomble, Head of the laboratories and Mr Collette must be mentionned.

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Mr Hambucken of C.O.P. and Mr Fober of C.N.R.M. were in charge of the apparatus. Without their constant care and zeal no success could have been achieved.

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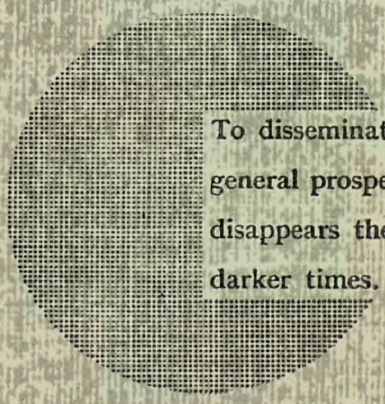

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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